

IN-SITU MODEL STUDIES OF METAL SULFIDE CATALYSTS

N.M. Rodriguez, and R.T.K. Baker
Chemical Engineering Department,
Auburn University
Auburn, AL 36849

Keywords: In-situ Electron Microscopy, catalytic hydrogenation of graphite, metal sulfide-hydrogen interactions

ABSTRACT

In-situ electron microscopy studies of the dynamic behavior of certain metal sulfides supported on single crystal graphite showed that when such specimens were treated in 0.2 Torr hydrogen, pitting of the carbonaceous support at edges, steps and defect regions of the basal plane occurred. In the absence of a catalyst attack of graphite by molecular hydrogen was not observed until the temperature was raised to above 1000°C. In contrast, when a metal sulfide was present gasification of the graphite took place at very low temperatures. We believe that this unusual behavior, which is quite different to that observed in the presence of metal catalysts, is the result of attack by atomic hydrogen which is produced from the interaction of molecular hydrogen with the metal sulfide particles. These observations are consistent with those of other workers who have studied the interaction of microwave generated atomic hydrogen species with graphite.

INTRODUCTION

Over recent years a considerable wealth of knowledge has been amassed on the manner by which catalysts can modify both the rate and selectivity of various reactions involving the conversion of petroleum feedstocks into a variety of fuel fractions and chemicals. There are tremendous opportunities available if one can learn how to exploit the potential of these petroleum-related catalyst systems to manipulate the decomposition of coal to produce a similar spectrum of speciality chemicals. Of particular importance with regard to the conversion of carbonaceous solids such as coal to high molecular weight hydrocarbons are the catalytic reactions involving hydrogen. In this context, it is well worth considering the phenomenon of migration or "spillover" of adsorbed species which is known to occur with certain supported metal catalysts systems. Perhaps the most widely known example of spillover behavior is that associated with dissociation of molecular hydrogen over certain metal catalysts.

The phenomenon of hydrogen spillover was first suggested from the observations that the rate of decomposition of GeH_4 to Ge was accelerated in the presence of platinum¹. The effect was also demonstrated by very elegant experiments in which the transformation of WO_3 to HxWO_3 during treatment in hydrogen in the presence of $\text{Pt/Al}_2\text{O}_3$ induced a color change from yellow to blue². Hydrogen spillover also appears to play an important role in the extent of reduction of a titanium oxide support when platinum was introduced onto this material and the system heated in hydrogen^{3,4}. Early work by Boudart and coworkers⁵ showed that hydrogen spillover from platinum to carbon occurred at 350°C and subsequently it has been demonstrated that this behavior can lead to methanation of the solid carbon⁶⁻⁸. Although the nature of the diffusing species is not yet established, it does appear that atomic hydrogen could be involved in the reaction mechanism.

The concept of using atomic hydrogen to convert carbonaceous solids to an assortment of hydrocarbon products has been reported by a number of workers⁹⁻¹⁸. In these studies hydrogen atoms were generated either in low pressure microwave discharge systems or by dissociation of molecular hydrogen over a hot tungsten filament. There is general agreement that the interaction of atomic hydrogen with carbonaceous solids can take place at a relatively rapid rate even at room temperature. On the other hand, a wide variation in the hydrocarbon product distribution and composition has been reported from such reactions, which appears to be related to the type of discharge system used to produce atomic hydrogen, the hydrogen pressure and the time of exposure. Vastola and coworkers¹¹ and later Gesser and Czubryt¹⁸ found that acetylene and methane were the major products with minor amounts of ethane, methylacetylene and pentane arising from the reaction of atomic hydrogen with graphite. In another study, Gill and coworkers¹⁰ produced hydrogen atoms by dissociation of H₂ over a tungsten filament and allowed these atoms to react with a carbon solid at 77K. At low pressure conditions methane, ethane, propane and butene along with an identified higher molecular weight compound were produced from the reaction with graphite. In contrast only methane and ethane were formed at higher pressures when helium was added to the hydrogen.

Form this brief overview of the interaction of atomic hydrogen species with coals and carbons it is clear that this approach holds a great deal of potential for the conversion of such solids into a variety of extremely useful precursor hydrocarbon molecules. The notion of producing atomic hydrogen via various discharge techniques is extremely interesting and offers the opportunity of controlling the energy of the atomic species, however, this experimental approach is fraught with technical difficulties when one attempts to scale up such a reactor system. The question which arises is can we perform such reactions by generating atomic hydrogen species from a somewhat simpler route, i.e. by catalytic dissociation of molecular hydrogen.

The characteristics of a suitable candidate for this operation would be one which has the capacity to dissociate molecular hydrogen in a reversible manner at relatively low temperatures. Examination of the literature shows that while the majority of metals are capable of dissociating molecular hydrogen, they do not readily release the atomic species. In contrast, it appears that certain metal sulfides and in particular molybdenum disulfide may well possess the desired characteristics¹⁹.

In the current study we have used the technique of controlled atmosphere electron microscopy to directly observe the behavior of hydrogen on two types of model catalyst systems:

- (a) cobalt supported on graphite, and,
- (b) molybdenum disulfide on graphite.

These two catalyst systems were found to exhibit dramatic differences in their behavior towards hydrogen and reasons for these observations are discussed.

EXPERIMENTAL

The experiments reported here were performed using a modified JEOL 200CX TEM electron microscope. This instrument is equipped with a custom designed environmental cell, which accommodates a heating stage. Specimens can be heated

up to a temperature of 1000°C while at the same time being exposed to a gas environment at pressures up to 3.0 Torr. The resolution of this instrument when used in conjunction with a closed-circuit television system is of the order of 0.4 nm.

Transmission specimens of single crystal graphite and molybdenum disulfide were prepared by a standard cleaving technique. Two procedures were used to prepare molybdenum disulfide/graphite specimens. In the first method, the sulfide was introduced onto the graphite in the form of particles from an ultrasonic dispersion of the powder in iso-butanol. In a second approach, transmission sections of both materials were mounted side by side on nickel grids. Cobalt was deposited onto the graphite substrates by evaporation of spectrographically pure wire from a tungsten filament at a residual pressure of 10^{-6} Torr. The conditions were selected so as to produce a film of metal at least one atom on average thickness. The reactant gas, hydrogen, was 99.999 % pure and used without further purification.

RESULTS AND DISCUSSION

(a) Cobalt/Graphite - Hydrogen

When cobalt/graphite specimens were heated in the presence of 0.2 Torr hydrogen, the deposited metal film was observed to nucleate into discrete particles at 350°C. On continued heating particles located on the graphite edge and steps sites were seen to exhibit dramatic changes in their wetting characteristics with the substrate and this behavior was reflected in a change in the mode by which they operated during the subsequent hydro-gasification reaction. This sequence of events is depicted schematically in Figure 1. At 400°C, particles were found to undergo a wetting and spreading action along the graphite prismatic faces. This behavior preceded the onset of catalytic attack at 450°C, which took place by the edge recession mode. It was interesting to find that the receding edges were aligned in particular directions, being parallel to the $\langle 11\bar{2}0 \rangle$ crystallographic orientations of graphite.

At 650°C, the catalyst exhibited a modification in its wetting properties with the graphite, which resulted in the re-formation of particles. This transformation was accompanied by a change in the mode of catalytic attack from edge recession to channeling. During channeling the active particles maintain contact with the graphite interface and as a consequence during propagation across the basal plane, always remain at the leading face of the channel. Quantitative kinetic measurements of a number of channeling sequences showed that the typical propagation rates exhibited by 25 nm diameter particles at 840°C was of the order of 10 nm/sec. A survey of many regions of the specimen revealed that the majority of channels were straight and oriented parallel to the $\langle 11\bar{2}0 \rangle$ graphite crystallographic directions.

It is possible that the observed change in wetting characteristics of the metal particles on the graphite which takes place at 650°C is a result of carbon being dissolved in the metal particles, and this event is known to induce changes in the interfacial energy of such particles²⁰. Previous studies with other metals have shown that although this behavior appears to be a general phenomenon²¹, the temperature where such transformations occur vary with each system. Finally, it is clear that in this type of catalyzed hydro-gasification reaction the removal of carbon atoms to form methane only occurs at the catalyst/graphite interface, there being no evidence for loss of carbon from regions devoid of catalyst material at temperatures below 1000°C.

(b) Molybdenum Disulfide/Graphite - Hydrogen

Treatment of graphite specimens containing particulates of molybdenum disulfide, in 0.2 Torr hydrogen produced some very unusual effects. Inspection of the graphite surface showed that even at room temperature erosion of certain regions of the basal plane was taking place. This took the form of the creation of very tiny pits (~ 3 nm width), which initially tended to form as discreet clusters. On continued reaction at the same temperature these pits expanded along certain directions and developed into single larger pits, about 10 nm in width, which adopted an hexagonal outline with an internal island of carbon. This sequence of events is shown in the schematic diagram, Figure 2. As the reaction proceeded it became apparent that the formation of pits was not restricted to regions in the immediate vicinity of the sulfide particles. Indeed, they tended to preferentially occur at surface imperfections on the graphite basal plane such as vacancies, steps and along twin bands. Other workers^{22,23} have used the gold decoration technique to demonstrate that atomic hydrogen species can attack the basal plane regions of graphite to produce monolayer pits. Such features would not be observed in the present experiment since the contrast difference afforded by conventional TEM does not allow one to distinguish differences in thickness down to this level.

It is difficult to rationalize these extraordinary observations without invoking the participation of very reactive species such as atomic hydrogen which is produced by dissociation of molecular hydrogen on the sulfide catalyst. The pattern of behavior found in this work is consistent with that reported by other workers who have studied the interaction of microwave generated atomic hydrogen species with graphite. The finding that attack of the graphite surface could take place at regions remote from the catalyst particles suggests that the active entities have the ability to migrate across the graphite surface to active sites via a "spillover" mechanism. Initial concern that the electron beam might be exerting some influence on the reaction was dispelled in subsequent experiments by performing blank experiments in which specimens were reacted in hydrogen in the absence of the beam for periods of up to 2 hours. When such specimens were eventually examined it was clear that there had been extensive reaction prior to exposure to the beam.

On raising the temperature to 100°C the attack became indiscriminate in nature so that the whole surface gradually acquired a textured appearance. Also at this time, it was evident that the initially formed pits were tending to lose their faceted outline and become more circular in shape reaching diameters of 40 nm. In many cases, as pits expanded they merged into adjacent ones with a result that vast areas of the graphite surface were progressively removed.

The intensity of the reaction increased perceptibly at 200°C and it was significant to find that over prolonged periods at this temperature a carbonaceous deposit started to accumulate on the surface with the result that in some cases it was difficult to resolve the presence of shallow pits that had been previously apparent at lower temperatures. This observation suggests the possibility that some of the graphite is undergoing hydrogasification to produce hydrocarbons other than methane, which are susceptible to decomposition in the presence of the electron beam. At 350°C the reaction became so extensive that under these conditions the surface acquired a holey structure and experiments were normally terminated as the graphite specimens gradually lost their integrity.

In a further series of experiments the form of the specimen was changed to that where the molybdenum disulfide and graphite components were physically separated from one another. When this combination was reacted in 0.2 Torr hydrogen then attack of the pristine graphite surface was once again observed at room temperature. The subsequent behavior of these specimens was identical to that described above. The finding that it is not necessary for the catalyst to be in direct contact with the carbonaceous solid in order to promote hydro-gasification suggests that at the gas pressures used in these experiments it is possible for the active species to be transported through the gas phase in addition to the surface migration route.

ACKNOWLEDGMENTS

Financial work for this research was provided by the United States Department of Energy, Basic Energy Sciences, Grant DE-FG05-89ER14076 and CFFLS program Contract No DE-FC22-90-PC90029

REFERENCES

1. Taylor, H. S., *Ann. Rev. Phys. Chem.*, **5**, 646 (1967).
2. Khoobiar, S., *J. Phys. Chem.* **68**, 411 (1964).
3. Baker, R. T. K., Prestridge, E. B., and Murrell, L. L., *J. Catal.* **79**, 348 (1983).
4. Dumesic, J. A., Stevenson, S. A., Sherwood, R. D., and Baker, R. T. K., *J. Catal.* **99**, 79 (1986).
5. Boudart, M., Aldag, A. W., and Vannice, M. A., *J. Catal.* **18**, 46 (1970).
6. Tomita, A., and Tamai, Y., *J. Catal.* **27**, 293 (1972).
7. Olander, D. R. and Balooch, M., *J. Catal.* **60**, 41 (1979).
8. Chang, T. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **123**, 486 (1990).
9. Blackwood, J. D., and McTaggart, F. K., *Aust. J. Chem.*, **12**, 533 (1959).
10. Gill, P. S., Toomey, R. E., and Moser, H. C., *Carbon* **5**, 43 (1967).
11. Vastola, F. J., Walker, Jr., P. L. and Wightman, J. P., *Carbon* **1**, 11 (1963).
12. Wood, B. J., and Wise, H., *J. Phys. Chem.* **73**, 1348 (1969).
13. McCarroll, B., and McKee, D. W., *Carbon*, **9**, 301 (1971).
14. Sanada, Y., and Berkowitz, N., *Fuel*, **48**, 375 (1969).
15. Amano, A., Yamada, M., Shindo, T., and Akakura, T., *Fuel* **63**, 718 (1984).
16. Amano, A., Yamada, M., Shindo, T., and Akakura, T., *Fuel* **64**, 123 (1985).
17. Wong, C.-L. Chen, C.-W. and Timmons, R. B., *Fuel* **65**, 1483 (1986).
18. Gesser, H. D., and Czubyrt, J. J., *Fuel* **67**, 375 (1988).
19. Wright, C. J., Sampson, C., Fraser, D., Moyes, R. B., Wells, P. B. and Riekel, C., *J.C.S. Faraday I* **76**, 1585 (1980).
20. Weisweiler, W., and Mahadevan, V., *High Temp.-High Pressures* **4**, 27 (1972).
21. Baker, R. T. K., in "Carbon and Coal Gasification" (Eds. Figueiredo, J. L., and Moulijn, J. A.) Martinus Nijhoff Publishers, The Netherlands, 231 (1986).
22. Chen, J. P. and Yang, R. T., *Surf. Sci.* **216**, 481 (1989).
23. Pan, Z. J., and Yang, R. T., *J. Catal.* **123**, 206 (1990).

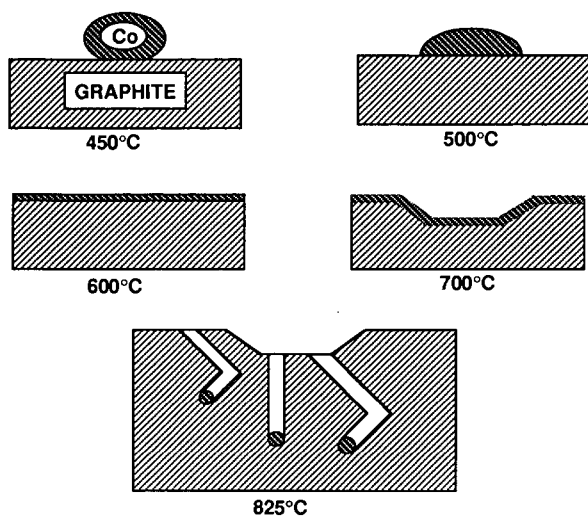


FIGURE 1. Change in wetting properties of a particle on graphite and the concomitant modification in catalytic action.

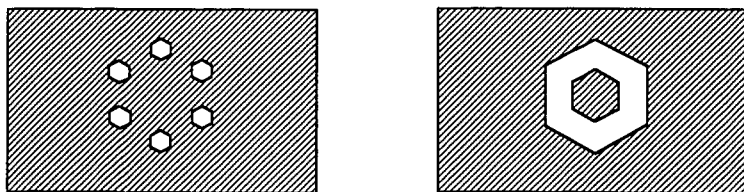


FIGURE 2. Development of pits in graphite from interaction with atomic hydrogen